PB-228 534

LABORATORY INVESTIGATIONS NO. 1

F. E. DeMartini

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

24 June 1963

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 228 534

LABORATORY INVESTIGATIONS NO. 1

HE 20.1011
X1-1

Technical Advisory & Investigation Section

Technical Services Branch

Division Of Water Supply And Pollution Control

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

U.S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE

Public Health Service

Robert A. Taft Sanitary Engineering Center

Cincinnati, Ohio

HE 20.1011
X1-1

LIBRARY
Environ. Prot. Agency, WPO
Edison, New Jersey 08817

35

OPTIONAL FORM NO. 10
5010-104

UNITED STATES GOVERNMENT

Memorandum

Robt. A. Taft Sanitary Engineering Center
4676 Columbia Parkway, Cincinnati, Ohio

TO : Chief, Water Projects Section, PHS
Regional Program Directors, PHS
Directors of Field Projects, PHS

DATE: June 24, 1963

FROM : F. E. DeMartini, Chief
Technical Advisory & Investigations Section
Technical Services Branch, DWSPC

SUBJECT: Report of Laboratory Investigations

The studies reported herein were conducted in the laboratories of the Technical Advisory and Investigations Section, Technical Services Branch. They are part of a continuing evaluation of present and proposed equipment and methodology.

This report is forwarded for your information and covers investigations on:

1. Sargent Polarographic Oxygen Analyzer
2. Thermo-Fishometer Water Thermometer
3. Modified Methods for Turbidity
4. Modified Methods for Color
5. Suspended Solids Determination

1. The Sargent Analyzer, employing a modification of the polarographic DO determination, was found to give a mean error of approximately 1 mg/l. The error was primarily due to the design of the sample transfer system.

2. Although the remote thermistor instrument had a mean error of 0.7° C., it was considered satisfactory for most routine stream survey work.

3. The Jackson Candle procedure for turbidity is cumbersome and crude. Instrumental methods such as the Spectrophotometer and the Hellige Turbidimeter have been suggested. These studies show that, due to light-scattering, neither instrument performed satisfactorily as a substitute for the Candle Turbidimeter.

LIBRARY

4. Color determination by Spectrophotometer was also found to be unsatisfactory. The study disclosed, however, that the filtrate from the suspended solids determination could be used for color measurement. The membrane filter was not satisfactory for suspended solids removal.

5. The study of the suspended solids determination indicated that the failure to secure a representative sample was the principal source of error. The standard deviation of the determination was $\pm$ 10% when domestic sewage was the sample.

EVALUATION OF SARGENT POLAROGRAPHIC OXYGEN ANALYZER

I. PURPOSE OF STUDY

Because of the importance of DO analysis in water, a series of performance tests were conducted on the Sargent Polarographic Oxygen Analyzer to determine its effectiveness as an instrument to measure oxygen concentration.

II. DESCRIPTION OF INSTRUMENT

The Sargent Polarographic Oxygen Analyzer is a portable unit designed to give an "on-the-spot analysis" for oxygen in natural and effluent waters. It operates on a polarographic principle, utilizing a horizontally mounted rapid dropping mercury electrode. See Figure 1.

The sample, collected in a standard BOD bottle, is siphoned into an electrolysis vessel. The DO is polarographically reduced and the resulting current measured. The DME is supplied with mercury from a reservoir. The anode is a mercury pool with electrical contact through a platinum foil electrode. A Thermometer is mounted in the cell. A quarter pound of potassium chloride is stored above the panel.

The panel consists of a meter, two switches and an applied potential control. The meter serves as both voltmeter and microammeter. Current readings are taken directly, and voltage readings

can be obtained by dividing the scale by ten. Directly beneath the meter is a power switch, which must be in the ON position during operation. The switch adjacent to the power switch converts the microammeter to a voltmeter. The applied voltage is adjusted by means of Applied Potential Control.

III. TEST PROCEDURES

The polarographic oxygen analyzer must be calibrated each day prior to a sample analysis. The calibration procedure is as follows:

A sample of water is obtained in the sample bottle, and 3 measures of KCl are added. The sample is siphoned into the electrolysis vessel, completely covering the DME. The sample is then saturated with oxygen from air, and the Applied Potential set of 1.6 volts. Current and temperature of the sample are recorded. The sample is purged with nitrogen, and the current reading again recorded.

To analyze a DO sample, the sample is collected in a standard BOD bottle. Three measures of KCl are added and mixed. The Applied Potential is adjusted to 1.6 volts. The sample is siphoned into the electrolysis vessel, and current and temperatures are measured and recorded. The oxygen concentration is calculated from the calibration curve.

In testing the instrument, a range of DO values was obtained in the samples by bubbling nitrogen through tap water.

A total of 54 sets of duplicate samples in BOD bottles were collected. At each DO level, the oxygen concentration was determined polarographically and by the Azide modification of the Winkler method.

IV. TEST RESULTS

Table I, and Figure 2, illustrate comparisons in DO concentrations by the Azide modification of the Winkler method and the polarographic method, with corresponding deviations. Minimum deviation was 0.04 mg/l, maximum deviation 2.94 mg/l, and mean deviation was 0.97 mg/l DO.

Table II shows that, as the DO decreases, greater error in oxygen measurement occurs due to aeration of the sample. Polarographic DO values are widely scattered at lower DO levels.

The curves show similar comparison in DO values obtained by the polarographic method and the Winkler Azide method. Note that deviation is greater, due to aeration of sample, as DO deficit increases.

V. SUMMARY

Based on data obtained through instrument performance, the following conclusions were made:

1. The Polarographic Oxygen Analyzer, as it is now designed, is not sufficiently accurate for determination of dissolved oxygen.

2. When sample is transferred to electrolysis vessel, air bubbles enter siphoning tube from the sample bottle. DO concentration is increased by aerating the sample in the electrolysis vessel.

3. As DO deficit increases, effect of aeration becomes more significant, causing an increase in deviation from Winkler DO.

4. Sample does not siphon from the sample bottle uniformly.

5. Sometimes the sample does not cover the dropping mercury electrode in the sidearm. Electrical contact is prevented, giving an erroneous current reading.

6. Occasionally, the current being measured in the electrolysis vessel drifts downscale with time, giving a false DO reading.

7. In the lower DO range, aeration of sample in the electrolysis vessel increases the DO concentration considerably.

8. Upon calibration of the instrument, the residual current varies, causing an error in the DO reading.

VI. RECOMMENDATIONS

1. Siphoning speed should be reduced by using a smaller siphon tube or an adjustable clamp. This would eliminate the air introduced into the sample.

2. The dropping mercury electrode capillary should be placed lower in the sample inlet tube of the electrolysis vessel to insure that the sample completely covers it.

3. Too much mercury is used under the present conditions, therefore, re-use of the mercury would be advantageous.

4. A larger supply of potassium chloride should be on hand.

5. With the recommended changes in design and use, this instrument may be suitable for field DO determinations.

TABLE I

Winkler versus Polarographic DO

Winkler DO mg/l	Polarographic DO mg/l	Deviation
9.55	8.66	- .89
8.40	7.85	- .55
8.40	8.33	- .07
8.30	7.70	- .60
8.30	7.68	- .62
8.30	7.70	- .60
7.80	7.52	- .28
7.70	7.56	- .14
7.70	7.95	+ .25
7.65	7.36	- .29
7.50	7.46	- .04
7.30	7.00	- .30
7.20	7.08	- .12
7.10	6.99	- .11
7.00	7.19	+ .19
6.85	7.17	+ .32
6.70	7.00	+ .30
6.60	6.86	+ .26
6.30	7.20	+ .90
6.00	6.46	+ .46
5.50	5.65	+ .15
5.00	5.47	+ .47
4.80	5.85	+1.05
4.75	5.02	+ .27
4.60	5.77	+1.17
4.30	5.09	+ .79
4.30	5.48	+1.18
4.20	4.90	+ .70
4.15	4.58	+ .43
3.90	4.76	+ .86
3.70	5.21	+1.51
3.60	3.90	+ .30
3.60	5.69	+2.09
3.50	4.73	+1.23
3.35	5.08	+1.73
3.25	3.56	+ .31
3.20	3.97	+ .77
3.10	4.62	+1.52
3.10	4.97	+1.87
2.70	4.04	+1.34

Table I - Continued

Winkler DO mg/l	Polarographic DO mg/l	Deviation
2.70	3.83	+1.13
2.60	4.07	+1.47
2.45	4.65	+2.20
2.20	3.97	+1.77
2.20	4.70	+2.50
2.10	2.61	+ .51
2.10	5.04	+2.94
2.00	3.96	+1.96
1.90	3.20	+1.30
1.90	4.62	+2.72
1.50	4.22	+2.72
1.50	4.19	+2.69
1.50	2.28	+ .78
1.40	1.97	+ .57

Deviation

MEAN: 0.97 mg/l

MIN: 0.04 mg/l

MAX: 2.94 mg/l

TABLE II

Deviation versus DO

Polarographic DO mg/l	Deviation from Winkler
8.66	- .89
8.33	- .07
7.95	+ .25
7.85	- .55
7.70	- .60
7.70	- .60
7.68	- .62
7.56	- .14
7.52	- .28
7.46	- .04
7.36	- .29
7.20	+ .90
7.19	+ .19
7.17	+ .32
7.08	- .12
7.00	- .30
7.00	+ .30
6.99	- .11
6.86	+ .26
6.46	+ .46
5.85	+1.05
5.77	+1.17
5.69	+2.09
5.65	+ .15
5.48	+1.18
5.47	+ .47
5.21	+1.51
5.09	+ .79
5.08	+1.73
5.04	+2.94
5.02	+ .27
4.97	+1.87
4.90	+ .70
4.76	+ .86
4.73	+1.23
4.70	+2.50
4.65	+2.20
4.62	+1.52
4.62	+2.72
4.58	+ .43

Table II - Continued

Polarographic DO mg/l	Deviation from Winkler
4.22	+2.72
4.19	+2.69
4.07	+1.47
4.04	+1.34
3.97	+ .77
3.97	+1.77
3.96	+1.96
3.90	+ .30
3.83	+1.13
3.56	+ .31
3.20	+1.30
2.61	+ .51
2.28	+ .78
1.97	+ .57

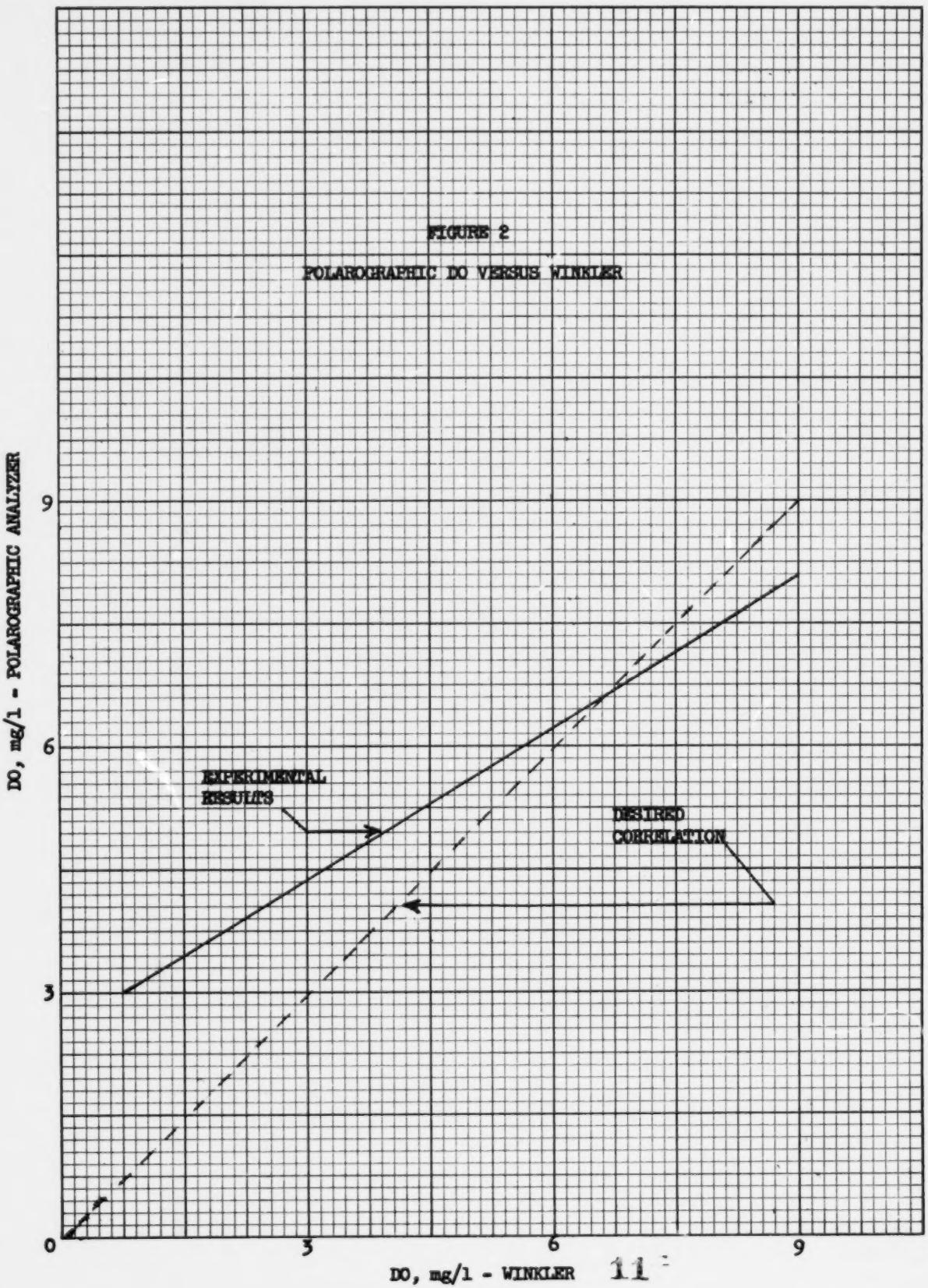
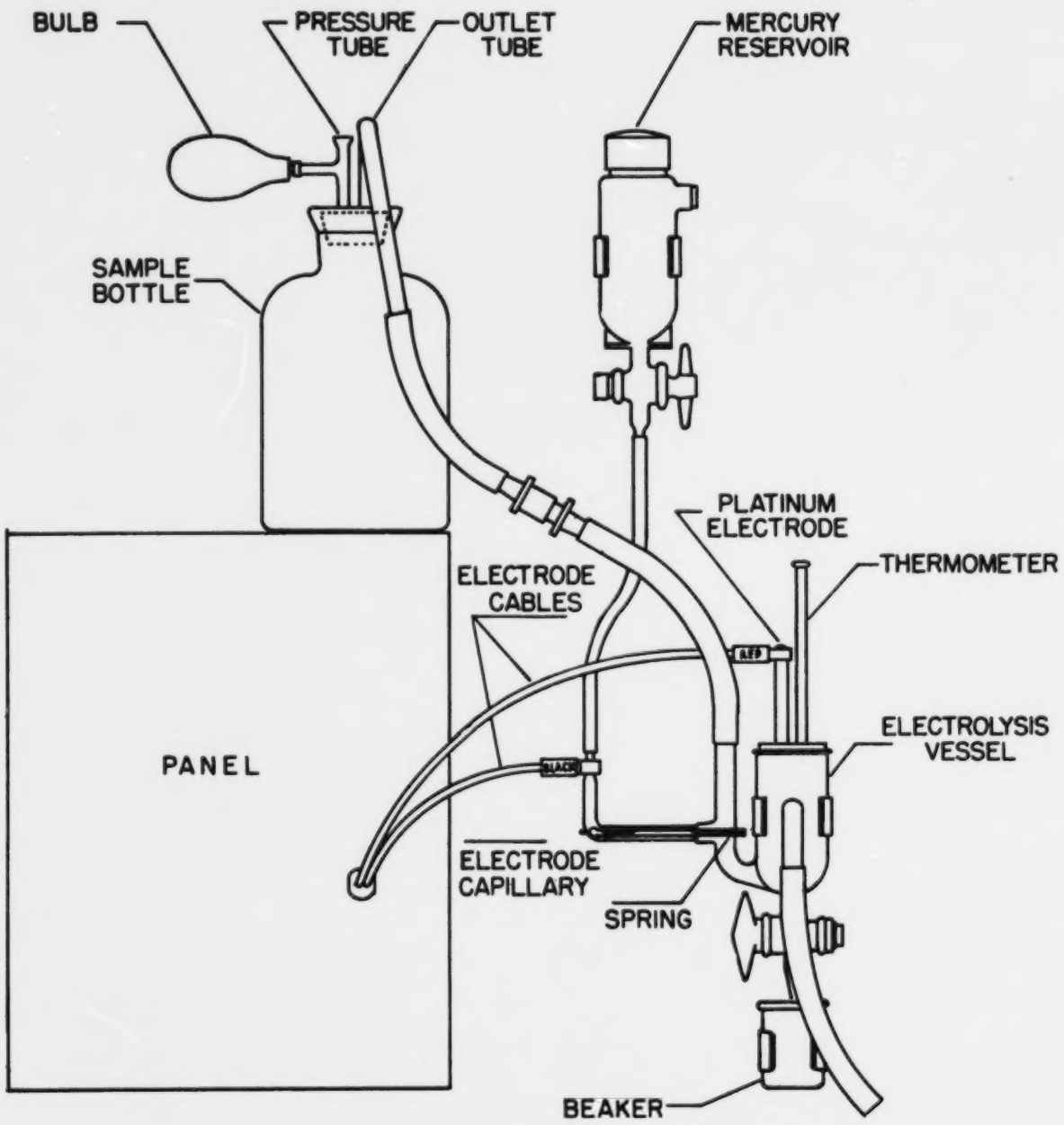


FIGURE 2
POLAROGRAPHIC DO VERSUS WINKLER
DO, mg/l - POLAROGRAPHIC ANALYZER
DO, mg/l - WINKLER
0
3
6
9
EXPERIMENTAL RESULTS
DESIRED CORRELATION



SARGENT POLAROGRAPHIC D.O. ANALYZER

EVALUATION OF INEXPENSIVE WATER THERMOMETER

In stream surveys, water temperatures at the time of sample collection are usually measured by inserting a metal thermometer into the sample bottle immediately after collecting. This technique, though yielding a reasonably reliable value, is subject to the criticism that the sample temperature may be increased or decreased by the temperature of the sampler, the sample bottle, or the ambient air temperature. When practicable, a more accurate water temperature should be obtained by measurement in the stream at sampling depth. The temperature measurement "in situ" is especially important when thermal stratification is present, as in cases of warm effluents entering colder receiving streams, or pronounced thermoclines in reservoirs.

Reliable thermistor instruments are commercially available for remote temperature measurements. Equipped with long (100 feet) lead-wire, these thermometers cost approximately $100.00. Recently a similar instrument, costing only $29.95, has become available. The unit is called the "Thermo-Fishometer" and is manufactured by:

Bright Radio Laboratories
222 East Second Street
Mineola, New York

According to the manufacturer, the thermometer is intended for use in fresh water only.

The unit is cylindrical, 3 1/2 inches in diameter and 6 inches long. Weight is approximately 1 1/2 pounds. The leadwire is wrapped on a reel, which fits into the case during storage but is fastened to the side of the instrument when in use (Figure 1). The dial is calibrated in degrees Fahrenheit ($^{\circ}$F) and degrees centigrade ($^{\circ}$C), although the indicating needle does not extend to the centigrade scale.

The thermistor is mounted in a plastic probe and is recessed for protection. The unit is supplied with 100 foot leadwire, marked at 5 foot intervals.

The thermometer unit was treated by immersing the probe in a circulating water bath, increasing the bath temperature from 5°C to 28°C and comparing the instrument readings against an accurate mercury thermometer. Comparisons are shown in Table I.

TABLE I

Fishometer Performance Data

Bath Temp., °C	Dial Reading, °C	Error, °C
27.9	28.9	+1.0
27.5	28.4	+0.9
26.0	26.5	+0.6
23.8	25.0	+1.2
22.1	21.8	-0.3
20.6	20.1	-0.5
19.2	21.8	+2.6
17.8	18.7	+0.9
16.0	15.1	-0.9
14.5	13.8	-0.7
13.0	12.3	-0.7
11.1	10.8	-0.3
10.1	10.0	-0.1
9.0	9.0	0
8.1	8.1	0
7.0	7.2	+0.2
6.0	6.5	+0.5
5.5	6.2	+0.7
5.4	6.4	+1.0

Mean Error: 0.7°C
Min. Error: 0°C
Max. Error: +2.6°C

The data indicate that the error is random over the range tested and that 17 of the 19 readings were within 1° of the true water temperature. During testing the lag time for a change of 20° was 4 seconds and no warm-up was required.

From the laboratory testing, the thermo-fishometer appears to be satisfactory for most routine water temperature measurements, although not sufficiently accurate for precise studies of thermal pollution.

THERMO - FISHOMETER

FIGURE 1

MODIFIED METHODS FOR TURBIDITY MEASUREMENTS

I. Purpose of Study

The standard procedure for the determination of stream turbidity is the Jackson candle method, as outlined in Standard Methods for the Examination of Water and Waste-Water. The method is awkward, lacks precision, and is time consuming.

Standard Methods states that instruments can be pre-calibrated against the Jackson candle turbidimeter and then used to determine turbidity. However, as it also states, the results obtained with such instruments will not always agree with the values obtained with the Jackson candle turbidimeter.

A better method was sought emphasizing photometric instruments. An instrumental method would be less tiresome, faster, and probably even more accurate. The purpose of this study was to evaluate proposed instrumental methods.

II. Test Procedures

Two instruments used in this study were the Hellige turbidimeter and the Bausch and Lamb Spectronic-20 spectrophotometer. These instruments were calibrated using the Jackson candle turbidimeter. Fuller's earth was used to prepare all turbidity standards.

The Spectronic-20 was calibrated at wave lengths of 420 mμ and 525 mμ. The 420 mμ wave length was selected because the Fuller's earth turbidity standards are similar to the turbidity of the $BaSO_4$ in the sulfate test. In the turbidimetric method for sulfate, a wave length of 420 mμ is used. The 525 mμ wave length was selected from the absorption spectrum of a stream sample filtrate. Several spectra from different stream samples produced maximum absorbance at that wave length. It was anticipated that turbidity values obtained on colored stream samples would have to be corrected for color.

After calibration with Fuller's earth standards, the turbidity was determined on six stream samples using the Jackson candle turbidimeter, the Hellige turbidimeter and the Spectronic-20. Color corrections were made on the results obtained with the Spectronic-20 at both wave lengths.

To correct for color, the samples were filtered through asbestos mats and the optical density of the filtrate subtracted from the optical density of the unfiltered sample. The corrected absorbance was then due to turbidity only.

III. Test Results

Table I

Jackson Candle versus Hellige Turbidimeter

Sample	Jackson Candle	Hellige	Difference
O-1	33	52	+19 (58%)
C-3	25	36	+11 (44%)
EP-1	25	41	+16 (64%)
E-9	750	960	+210 (28%)
CW-4	125	106	-19 (15%)
AM	28	60	32 (114%)

1) Jackson candle values can normally be reproduced within $\pm$ 10%. When compared to the Jackson candle method, the error of all samples was greater than 10%. Half of the samples are more than 50% in error and one more than 100% in error. Five of the samples gave results significantly higher than the Jackson candle reading.

2) It is apparent that even though data can be reproduced with the Hellige instrument the results are not correlative with the Jackson candle. Based on these studies the Hellige turbidimeter is not a satisfactory substitute for the Jackson candle turbidimeter for the determination of turbidity in stream samples.

Table II

Jackson Candle versus Spectrophotometer

Sample	Jackson Candle	420mμ Photometric	Difference	Color Corrected Photometric 420mμ	Difference
O-1	33	59	+26(79%)	54	+21 (64%)
C-3	25	38	+13 (52%)	28	+3 (12%)
EP-1	25	132	+107 (428%)	59	+34 (136%)
E-9	750	1180	+430 (57%)	1090	+340 (45%)
CW-4	125	149	+24(19%)	138	+13 (10%)
AM	28	54	+26(93%)	46	+18 (64%)

1) At a wave length of 420 mμ all 6 of the stream samples gave results greater than 10% in error and one was 428% in error. All values were higher than the Jackson candle readings.

2) When color correction was applied the per cent error was reduced significantly. The error of 2 of the 6 samples was reduced to about 10%.

3) Based on these studies the spectrophotometer, used at a wave length of 420 mμ, is not satisfactory for the determination of turbidity of stream samples, even when color correction is applied.

Table III

Jackson Candle versus Spectrophotometer

Sample	Jackson Candle	525 mμ Photometric	Difference	Color Corrected Photometric 525 mμ	Difference
O-1	33	51	+18 (54%)	49	+16 (48%)
C-3	25	33	+8 (32%)	27	+2 (8%)
EP-1	25	62	+37 (148%)	50	+25 (100%)
E-9	750	1000	+250 (33%)	965	+215 (29%)
CW-4	125	164	+39 (31%)	158	+33 (26%)
AM	28	61	+33 (118%)	58	+30 (107%)

1) At a wave length of 525mμ all 6 of the stream samples gave results greater than 10% in error. Half of these samples are more than 50% in error. Again, all valves were higher than the Jackson candle readings.

2) When color correction is applied, only one sample falls into the accepted limit of less than 10% deviation.

3) Based on these studies the spectrophotometer, used at a wave length of 525 mμ, is not satisfactory for the determination of turbidity of stream samples. Color correction does not materially change the accuracy of the instrument.

IV. Conclusions

Results obtained with the Hellige turbidimeter and the spectrophotometer were not correlative to Jackson candle values; therefore, the photometric instruments are not satisfactory for the determination of turbidity on stream samples. Errors are probably due to color in the sample.

The color interference is a combination of the substances in solution and the suspended matter. A photometric instrument that measures reflectance rather than transmittance might well be better. Standard Methods mentions nephelometers. It is suggested that nephleometers be investigated to determine their feasibility for turbidity measurement.

MODIFIED METHODS FOR COLOR DETERMINATION

I. PURPOSE OF STUDY

The accepted method for the determination of color in water samples, as outlined in Standard Methods for the Examination of Water and Wastewater, is to centrifuge the sample, if it has turbidity, and then compare visually with platinum-cobalt standards. Our practice has been to centrifuge turbid samples for twenty minutes before comparing with visual standards. A better method was sought for the removal of turbidity and color measurement with a photometric instrument was considered. The purpose was to save time in removing the turbidity and to gain accuracy through the use of a spectrophotometer.

II. TEST PROCEDURES

An absorption spectrum was determined on a platinum-cobalt standard (100 units of color) using a five centimeter cell in a Beckman Model B spectrophotometer. From the spectrum a wave length of 440mμ was selected for the measurement of absorbance of the color standards. A calibration curve was then obtained using color standards from 0-500 units.

Samples were centrifuged in an International Clinical Centrifuge at 3600 rpm for twenty minutes.

Other equipment used in this investigation included: Gooch crucible with asbestos mat as used in determining solids, 50 ml matched Nessler tubes, membrane filter assembly as used in determining coliforms, and assorted glassware.

Twelve stream samples were used in this study. These samples were collected from widely separated regions of the Unites States.

Sample No.	Location
EP-1	Mouth of East Pearl River, Louisiana
P42.2	Pearl River, Louisiana
E-3	Etowah River, Georgia
E-9	Etowah River, Georgia
CH-8	Chattahoochee River, Georgia
C-2	Cub River, Idaho
B-0	Bear River, Utah
I-4	Industrial waste effluent - dairy waste
A	Animas River, Colorado
LM	Little Miami, Ohio
C-6	Coosa River, Georgia
H-2	Pearl River, Louisiana

The turbidity was removed by three methods: centrifuge, asbestos mat, and membrane filter. The color was then determined both visually and instrumentally.

III. TEST RESULTS

TABLE I

Turbidity Removal: Centrifuge versus Membrane Filter

Color Measurement: Visual

Centrifuge		Membrane Filter		
Sample No.	Units of Color	Sample No.	Units of Color	Difference
EP-1	33	EP-1	33	0
P42.2	37	P42.2	28	-9
E-3	8	E-3	7	-1
E-9	13	E-9	2	-11
CH-8	18	CH-8	15	-3
C-2	13	C-2	7	-6
B-0	17	B-0	13	-4
I-4	22	I-4	15	-7
A	10	A	7	-3
LM	18	LM	12	-6
C-6	12	C-6	7	-5
H-2	20	H-2	20	0

1) When compared to the standard procedure, 6 of the 12 samples gave results beyond the acceptable range of ± 5 units of color, making this an unacceptable method for removing turbidity.

2) Filtering the sample through the membrane filter removes part of the color. This removal can be attributed to the electrostatic attraction between color particles and filter.

TABLE II

Turbidity Removal: Centrifuge versus Asbestos Mat

Color Measurement: Visual

Centrifuge		Asbestos Mat		
Sample No.	Units of Color	Sample No.	Units of Color	Difference
EP-1	33	EP-1	33	0
P42.2	37	P42.2	33	-4
E-3	8	E-3	8	0
E-9	13	E-9	12	-1
CH-8	18	CH-8	17	-1
C-2	13	C-2	13	0
B-0	17	B-0	15	-2
I-4	22	I-4	18	-4
A	10	A	12	2
IM	18	IM	17	-1
C-6	12	C-6	10	-2
H-2	20	H-2	20	0

1) All of the results are within the range of $\pm$ 5 units of color indicating that the asbestos mat may be employed as an alternate method for the removal of turbidity.

TABLE III

Turbidity Removal: Centrifuge

Color Measurement: Visual versus Instrumental

Visual		Instrumental		
Sample No.	Units of Color	Sample No.	Units of Color	Difference
EP-1	33	EP-1	33	0
P42.2	37	P42.2	45	+8
E-3	8	E-3	5	-3
E-9	13	E-9	20	7
CH-8	18	CH-8	33	5
C-2	13	C-2	13	0
B-0	17	B-0	19	2
I-4	22	I-4	23	1
A	10	A	15	5
LM	18	LM	27	9
C-6	12	C-6	11	-1
H-2	20	H-2	36	16

1) Four of the twelve results are beyond the range of $\pm$ 5 units of color and three of these are 50% or more in error. It is apparent that the spectrophotometric measurement is not satisfactory for the determination of color in stream samples.

TABLE IV

Turbidity Removal: Centrifuge versus Asbestos

Color Measurement: Visual versus Instrumental

Centrifuge-Visual		Asbestos Mat-Instrument		
Sample No.	Units of Color	Sample No.	Units of Color	Difference
EP-1	33	EP-1	35	2
P42.2	37	P42.2	44	7
E-3	8	E-3	10	2
E-9	13	E-9	25	12
CH-8	18	CH-8	28	10
C-2	13	C-2	15	2
B-0	17	B-0	20	3
I-4	22	I-4	27	5
A	10	A	28	18
IM	18	IM	42	24
C-6	12	C-6	37	25
H-2	20	H-2	37	17

1) Seven of the twelve samples are beyond the acceptable range of + 5 units of color, thus the asbestos mat--instrument system--would not be acceptable for color determination.

2) The spectrophotometer is very sensitive to the turbidity that is not removed by the asbestos mat. Note that all the values obtained with the spectrophotometer are higher than the centrifuge-visual values.

IV. CONCLUSIONS

These studies indicate that the membrane filter method for removing turbidity is not acceptable, but filtration through an asbestos mat is satisfactory. This latter is particularly advantageous when suspended solids are to be determined on the same sample. Part of the filtrate may be set aside for color determination.

Minute amounts of turbidity left in the sample prohibit the use of a spectrophotometer for color measurement. The membrane filter does remove this small amount of turbidity; however, a significant amount of color is also removed.

PRECISION OF SUSPENDED SOLIDS DETERMINATION ON SEWAGE SAMPLES

I. PURPOSE OF STUDY

The suspended solids determination of sewage, or "Total Suspended Residue" as it is called in Standard Methods, is subject to several sources of error. These are:

1. Failure to secure a representative aliquot of the sample.
2. Mechanical losses in filtration and drying.
3. Variation in volatility of solids.
4. Errors in weighing.

Standard Methods states that the precision of the determination is 1.4 mg. standard deviation of the weighing. That is, if a 100 ml. aliquot is filtered, the standard deviation is $\pm$ 14 mg/l, while if an aliquot of 50 ml. is filtered the standard deviation becomes $\pm$ 28 mg/l, and an aliquot of 25 ml. would result in a variation of as much as $\pm$ 56 mg/l. Since no absolute standard is available for comparison, the accuracy of the determination on sewage cannot be stated.

Experience in our laboratory, as well as reports from other workers, indicated that, with many sewage samples, filtering aliquots of 50 ml. or more is impractical. In order to determine the reliability of the solids procedure as routinely performed in our own laboratory, a study of the reproducibility of the determination was made.

II. TEST PROCEDURES

A sample of raw sewage was obtained and 10 replicate determinations were run, using 25 ml. aliquots.

III. TEST RESULTS

Table 1

	TSS 10	TVSS 10	%VSS 10
No. Replicates			
Mean (mg/l)	224	206	91%
Standard Deviation (mg/l)	± 47	± 47	± 3.4%
% of Mean (Relative Dispersion)	± 21%	± 23%	± 3.7%
Range of Values	170-308	156-300	87-97%

It is apparent that the procedure is not very precise and that approximately 2/3 of the time the values may vary as much as ± 20%. The reproducibility of the %VSS, however, is striking. The figures verify the fact that the chemical composition of the sample did not change and also indicate that the total variation due to mechanical losses and weighing errors is approximately 4% of the mean. We may conclude that the principal source of error in the method lies in the failure to secure a truly representative aliquot of the parent sample.

In order to confirm the conclusion a second set of determinations was made but the analyst was especially careful to mix the sample thoroughly and to remove the aliquots before settling occurred. The improvement in precision is shown in Table 2.

As a result of increased attention to reproducing the solids content of the individual aliquots, the standard deviation was halved for the total suspended solids and reduced by 2/3 for the volatile portion. It is significant to note that the %VSS precision was not improved in the second run, indicating that the better precision was due to the handling of the sample rather than more careful weighing.

Table 2

	TSS	TVSS	%VSS
No. of Replicates	10	10	10
Mean (mg/l)	242	170	71%
Standard Deviation (mg/l)	± 24	± 11	± 3.6%
% of Mean (Relative Dispersion)	± 10%	± 6.5%	± 5%
Range of Values	218-288	148-192	62-75%

IV. CONCLUSIONS

Based on the very limited data obtained in this study, the following conclusions may be drawn:

1. The principal source of error in the determination of total and volatile suspended solids in sewage is the failure to obtain a representative portion of the sample.

2. When sufficient attention is given to filtration of a representative aliquot, the precision of the method is approximately $\pm$ 10% of the TSS in mg/l.

3. In spite of the additional manipulation required to determine VSS, the values obtained for this parameter are as precise as the TSS concentration.

4. The %VSS is the most precise of the three values obtained by the suspended solids analysis.